Radiocarbon dating of medieval manuscripts from the University of Seville.

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Abstract

Eleven samples (parchment and paper) from different medieval manuscripts belonging to the cultural heritage of the University of Seville have been radiocarbon dated on the 1MV AMS facility at the CNA in Seville (Spain). The objective of this study is double. First of all, these are the first real "unknown" samples treated in the radiocarbon laboratory and dated on our AMS facility, SARA (Spanish Accelerator for Radionuclide Analysis). Besides, some useful information about the manuscripts can be obtained, either to corroborate the dates, or in some cases, to decide between possible dates. As expected, a general agreement is found between radiocarbon results and palaeographical data. Nevertheless, some interesting facts have been learned through this study. We present in this paper the procedure to prepare the samples and the ages obtained with a brief discussion of the results.

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Introduction

The General Library of the University of Seville was created in 1502 and opened to general public in 1843. Material was received from donations, inheritances and also bought using donated funds. Its present location dates from the 1950's when the University moved to the Real Fábrica de Tabacos. The Antique Section of the Library owns circa 800 manuscripts, more than 300 incunabula, and nearly 40000 volumes from the 16th-18th centuries, which form part of the cultural heritage of the University of Seville. They are preserved in a special security room under controlled conditions of temperature and humidity.

Palaeographical methods are commonly used in the study of medieval manuscripts in order to estimate the date of these valuable objects. These methods rely on the evolution of the art of writing and the different styles and decorative patterns, and are subject to geographical and cultural differences and, in general, spread in time. Thus, information obtained through palaeography gives usually wide age ranges. Unless there is some direct reference in the manuscript about the date, palaeography usually locates the writing style within a century. The use of radiocarbon dating by AMS provides the researchers with another tool to corroborate the findings of palaeographers, causing minimum damage to the manuscripts. Besides, radiocarbon dating is an absolute dating method.

Sample preparation and measurement

For this study, 10 manuscripts have been chosen from among the oldest ones found in the library. According to palaeographical studies, they are all estimated to belong to the 14^{th} or 15^{th} century. Two of them are more precisely dated due to the presence of text in the manuscript regarding the finishing year. Three of the manuscripts are written on paper, the other seven are written on parchment. A brief list of the samples is presented here in table 2 and in the Appendix, and a complete description of the manuscripts can be found in [1].

Samples were taken directly at the General Library. Clean, small fragments (typically 50 mg) were cut from the corner of one of the pages of the manuscript, avoiding stains or gelatinized parchment. Chemical preparation of the samples follows standard procedures described in [2] with small changes. Even though the samples apparently did not present any kind of preservatives or additives, soxhlet extraction was applied using hexane, acetone and ethanol before treating the samples with the Acid-Alkali-Acid cleaning procedure. Each organic solvent was applied for about 1 hour. For the AAA procedure HCl 0.5M and NaOH 0.1M were used, and time was carefully controlled to avoid severe losses by dissolution. In general, each cleaning step lasted around 15 minutes. A first aliquot left for a longer time disappeared completely, which made us decide for shorter periods. Sample CNA205 was prepared a second time, named CNA205b, in which the cleaning consisted only in the first acid bath. No alkaline solution was added, in order to compare the results and see whether the use of all the steps was necessary or not.

Between 7-10 mg of clean and dry paper or parchment were combusted at 950 ºC for three hours in a vacuum sealed quartz tube with CuO and Ag powder. Quartz tubes had been previously baked at 950 ºC to eliminate possible organic matter. Produced CO_2 was then reduced to graphite by adding excess H_2 and using cobalt as catalyst. The resultant mixture of graphite and cobalt was pressed into aluminium cathodes and kept on vacuum until measurement [3].

Measurements were carried out at the 1MV AMS facility of the CNA, SARA [4]. Manuscript samples were measured in two different sets. CNA002 to CNA007 were measured in May 2007, and were part of the first set of unknown samples measured at the CNA AMS facility. After the first promising results, a second set of samples was selected to continue the study. CNA205 to CNA209 were measured in July 2008. Measurement procedure has been previously described [3,4]. Main parameters can be seen in table 1. For the first set of samples, measurement took place during 30 minutes, consisting of 6 individual measurements divided in 10 blocks of 30 seconds each. Individual measurements were alternated with standards and blanks. In the second set of samples, each block lasted 40 seconds, thus giving a total measurement time of 40 minutes.

Results

Results are shown in table 2 and on the graph. Calibration of the radiocarbon ages has been done using CALIB 5.0 [5,6].

As a general statement, we could say there is a good agreement between radiocarbon results and palaeographic estimations. In most cases, calibrated age distributions overlap the age range estimated for the manuscript. There are samples like CNA004 or CNA007 where the radiocarbon analysis does not really provide better information, because the age distribution overlaps over the whole estimated range. However, there are other samples where the radiocarbon age distribution delimits the original estimation, and besides, opens new possibilities. CNA005, CNA006 and CNA205 are examples of this situation. In these cases, it is clear that the radiocarbon analysis offers interesting information.

Two of the samples, CNA207 and CNA209, had a more definite age due to the information on the manuscripts. In particular, CNA207 was estimated to belong to the 15^{th} century, but with no doubt earlier than 1465, and CNA209 was known to be written between 1487 and1491. In both cases, radiocarbon results are in total agreement with previous knowledge.

Two other samples, CNA003 and CNA208, resulted in older age than estimated by palaeography. The shift in both cases is about one hundred years. One possibility is that these manuscripts are palimpsests, i.e., parchment was reused after washing the writing and scraping the surface of the parchment. This was a common practice in the Middle Ages because of the high price of parchment. However, this possibility is not mentioned in the bibliography [1]. It seems also unlikely that the parchment was not used for a long time. Meanwhile the CNA002 result was younger than predicted by palaeography. It does not seem to be a systematic shift in the procedure, and chemical contamination seems to be unlikely, since samples did not have any added preservatives and followed the whole cleaning process.

Samples CNA004 and CNA005 come from two differentiated parts of the same manuscript. The parchment in each part was clearly different, so there were doubts about the two samples being coetaneous. Radiocarbon results are very similar, suggesting that both parts of the manuscript may well be coetaneous.

CNA205 and CNA205b are aliquots of the same parchment sample, but treated in a slightly different way, with the second aliquot suffering only the first acid bath in the AAA cleaning procedure. They show nearly identical results. Although it is not a clear proof, it seems that in this kind of samples, it may be possible to reduce alkaline cleaning to a minimum, avoiding severe losses by dissolution.

Conclusions

Radiocarbon dating by AMS has been effectively applied to a set of valuable samples from manuscripts. Results prove that radiocarbon dating can help palaeography in the study of the origin of these manuscripts. The use of AMS for radiocarbon dating causes minimum damage to the manuscripts, and gives a fast and accurate tool to researchers to confirm palaeographical estimations.

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Appendix

List of the samples included in the study.

CNA002 (331-143) – *Crónica de los Reyes de España,* by Rodrigo Ximénez de la Rada, History, in Spanish.

CNA003 (331-221) – *Biblia Sacra Vulgata Latina*, Bible, in Latin .

CNA004 (331-222) – *De lingua latina. De disciplina originum verborum,* by Marco Terencio Varrón, Latin language, in Latin.

CNA005 (331-222) – *Stratagemata cum liber*, by Sesto Iulio Frontini, in Latin

CNA006 (332-108) – *Rubricas morales ex doctrina*, *Vol I*, Saint Jerome, Theology, in Latin.

CNA007 (332-111) – *Summa collectionum seu communi loquium; Expositio regulae San Agustini; Distinctiones*, by several authors, Augustinian order, in Latin.

CNA205 (330-154) – *Otto libri di Fisica*, by Aristotle, Natural philosophy, in Latin.

CNA206 (330-155) – By Demosthenes, in Greek.

CNA207 (331-173) – *De Rethorica*, by Aristotle, in Latin.

CNA208 (332-150-4) – *Bible*, Bible, in Latin.

CNA209 (332-155) – *De Animalibus, Questiones naturals*, by Aristotle, in Latin.

References

[1] Ángela Núñez Gaitán, “Manoscritti anteriori al XVI secolo nella Biblioteca Generale universitaria di Siviglia”, (1997) A F.A. 091:017/BUS, General Library of the University of Seville

[2] G. Bonani, S. Ivy, W. Wölfli, M. Broshi, I. Carmi, J. Strugnell, “Radiocarbon dating of fourteen Dead Sea Scrolls”, Radiocarbon 34(3) (1992) 843

[3] F.J. Santos, I. Gómez-Martínez, M. García-León, “Radiocarbon measurement programme at the Centro Nacional de Aceleradores (CNA)”, (2008) Radiocarbon and Archaeology 5th International Symposium, submitted to Radiocarbon.

[4] E. Chamizo, J.M. López-Gutiérrez, A. Ruiz-Gómez, F.J. Santos, M. García-León, C. Maden, V. Alfimov, “Status of the compact 1 MV AMS facility at the Centro Nacional de Aceleradores (Spain)”, Nucl. Instr. Meth. B266 (2008) 2217

[5] M. Stuiver, P.J. Reimer, (1993) Extended 14C database and revised CALIB radiocarbon calibration program, Radiocarbon 35(1) (1993) 215

[6] M. Stuiver, P.J. Reimer, R.W. Reimer, (2005) CALIB 5.0 [WWW program and documentation]

Figure Captions

Table1 - Measurement parameters for ^{14}C determination at SARA. Sigma values for HOxII are internal/external error respectively from a set of five cathodes. In the case of $^{13}C/^{12}C$ ratio only external error is considered. Stripper pressure is measured at the central point of the stripper tube.

Table2 - Manuscript samples included in the study. Signature refers to the code at the General Library.

Figure 1 - Results of the radiocarbon dating compared to the palaeography estimation of the samples. Discontinuous box represents the palaeographical dating. Radiocarbon dating is represented in black and white blocks for 1σ and 2σ calibration respectively.

Charge State	**Terminal Voltage**	**LE ^{12}C current**	**Transmission**	**Stripper pressure**
2+	1000 kV	20-25 μA	~43%	2×10^{-2} mbar
Sigma* for HOxII $^{14}C/^{12}C=1.30\times10^{-12}$	**Dependence of $^{13}C/^{12}C$ on current**	**Sigma $^{13}C/^{12}C$ (uncorrected)**	**Sigma $^{13}C/^{12}C$ (current corrected)**	**Chemical Blanks**
(0.14/0.18)%	$3\text{-}10\times10^{-6}/(\mu A\ ^{12}C)$	0.8 ‰	0.3‰	~ 7×10^{-15}

Lab Code	Signature	Material	$\delta^{13}C$(‰)	^{14}C Age (BP)	Calibrated Age (2σ)	Paleographic Dates
CNA209	332-155	Parchment	-23.23±0.32	400±30	1436-1521 AD (0.84) 1575-1582 AD (0.01) 1591-1622 AD (0.15)	1487-1491
CNA208	332-150-4	Parchment	-29.21±0.28	620±30	1293-1399 AD	15th century
CNA207	331-173	Paper	-27.26±0.29	465±25	1414-1454 AD	15th century, before 1465
CNA206	330-155	Paper	-27.15±0.29	460±30	1410-1471 AD	15th century
CNA205b	330-154	Parchment	-24.40±0.27	375±25	1446-1524 AD (0.65) 1558-1631 AD (0.35)	15th century
CNA205	330-154	Parchment	-25.21±0.25	370±25	1450-1524 AD (0.60) 1558-1631 AD (0.40)	15th century
CNA007	332-111	Parchment	-17.5±1.1	420±40	1419-1523 AD (0.81) 1571-1630 AD (0.19)	15th century
CNA006	332-108	Parchment	-20.4±1.0	410±45	1422-1527 AD (0.72) 1554-1633 AD (0.28)	14th-15th century
CNA005	331-222 (part B)	Parchment	-22.2±1.0	565±45	1299-1370 AD (0.57) 1380-1433 AD (0.43)	15th century

CNA004	331-222 (part A)	Parchment	-20.56±0.83	490±60	1301-1367 AD (0.17) 1382-1521 AD (0.79) 1591-1620 AD (0.04)	15th century
CNA003	331-221	Parchment	-25.09±0.84	760±45	1183-1296 AD	14th century
CNA002	331-143	Paper	-22.14±0.93	300±40	1477-1660 AD	15th century